Dear Francis,

We thank you for the time you invest in our manuscript. We have now revised the manuscript again and have hopefully addressed the remaining issues in a satisfactory manner. Please find our responses to the referee´s comments in italics. The revised manuscript contains changed in red.

Best regards,

Ramakrishna Ramisetty and co-authors

Report 1:

The authors satisfactorily addressed all questions raised during the peer-review process. I therefore recommend publication, after correction of a minor error and careful proof-reading of the changes introduced in the paper. The minor error to be corrected is: if we consider a velocity of 1000 m.s-1 (which is generally accepted), then indeed the ejecta will move 5 µm in 5 ns, but not 0.1 µm in 100 fs. 100 fs is 10^-13 s, this means the ions will move 0.1 nm (i.e. 1 A) during this time, and not 0.1 µm. Please correct accordingly in the text.

We thank the referee of report 1 for his or her positive assessment of our reviewed manuscript. The mentioned error is corrected as indicated..

Report 2:

The concerns in my original report have not been sufficiently addressed. I am unconvinced that the method for varying the power density for the fs layer system is valid with co-axial instrument geometry. The method relies on the ion extraction region and ion intensities to fix the ablation position. The ion extraction region is not defined and there is no evidence of how the ion intensity is related to the position within it. Furthermore, with the exception of PSL, there is still not enough data to support the qualitative description of the mass spectral patterns.

We think we have sufficiently explained how we defined the ionization region and hence the power density. However, for simplification reasons, and to hopefully make it easier to understand for our readers, we suggest a simplified Figure 9 that shows the dependency of ion signal on laser power density without the explicitly separating the two focus positions F1 and F2. The ranges of power densities induced by varying focus positions are reflected in the error bars of the figure. We note here that this does not affect our interpretation of results, and that the power density variation by changing the laser power is quite significant and clear. We have moved the initial Figure 9 into the SI (now Fig. S14), and added the following paragraph to section 3.2.1: "Fig. S14 shows the same data as Figure 1, but separated for focus positions F1 and F2. Note that for the fs-laser, due its free firing mode, the ionization position and corresponding power density is highly uncertain and represents a best estimate. Consequently, we cannot rule out an overlap between possible power densities corresponding to F1 and F2, respectively."

We consider the amount of data sufficient to support the interpretation of the mass spectral patterns. This is supported by the fact that we could reproduce similar mass spectral patterns at different dates also for particles other than PSL.

Report 3:

Mass spectra obtained from the LAAPTOF single-particle mass spectrometer using a conventional 193 nm excimer ns-pulse laser and a 800 or 266 nm Ti:Sapphire fs-pulse laser are presented. The objective appears to be to explore if the higher laser power density of a fs laser produces higher ion signal and more complete ionization of the entire particle. This would improve the quantitative abilities of SP-MS using LDI, which is hampered by particle matrix effects and the complex interactions between individual particles and the high energy laser pulse. This is certainly a worthwhile objective whose results will be of interest to readers of AMT. This main objective could have been more clearly presented upfront, and then discussed again as to its success or failure in the conclusions. While the results presented do not support this hypothesis or indicate good promise in the use of a fs-pulse for single-step LDI, the new findings still provide valuable information. The manuscript has already gone through one round of peer review and has improved during the revisions and rebuttal. There are a few key remaining areas that require better clarification and discussion, as well as some relevant references that should be added and discussed. While the scientific quality of the results and their discussion presented here is not high, these measurements required considerable resources and efforts to obtain. We can let the community decide for themselves if this is a worthwhile study. This manuscript should be acceptable for publication in AMT following minor revisions.

We thank referee #3 for his or her positive evaluation of the importance of our study. We have now clearly formulated the objective of the study and added this information to the abstract ("Its objective is to assess whether the higher laser power density of the fs-laser leads to a more complete ionization of the entire particle and higher ion signal, and thus improvement of the quantitative abilities of SPMS.") and the introduction ("In this study we explore the potential of high power density fs-laser pulses for improved quantitative abilities of SPMS."). In the conclusions section, we state clearly that "The idea, that the higher power density that can be achieved with fs-laser pulses leads to a more complete particle ablation and ionization, could not be substantiated in this study."

My major comment and confusion concerns the role of the LDI laser wavelength. The fs-pulse laser was operated at 800 or 266 nm. I would think the laser wavelength would have a huge influence on how the photons interact with the particle, since the complex index of refraction is a strong function of wavelength. While a multi-photon ionization process is involved, the 266 and 193 nm photons have much more energy than the 800 nm photons. I realise this issue was already brought up by reviewer #2, but this important topic is still not addressed satisfactorily.

We regret to not have addressed the topic of LDI laser wavelength sufficiently in the revised version of our manuscript, and hope to clarify this in the new version. We agree that the ionization laser wavelength can have an important impact on laser desorption and ionization, as we state at several occasions in the manuscript (e.g. introduction or section 3.1.5). However, in our study we did see only surprisingly small differences for single particle mass spectra obtained for the different wavelengths (new Figs. S7 – S13 in the SI). Therefore, and to limit the complexity of the manuscript, we did not show all results for all wavelengths, but focus on fs-laser spectra at 800 nm (default wavelength) in the main manuscript. In addition, the application of a third harmonic generation module from Spectra Physics® (model TP-THG-F) to lower the fs-laser wavelength to 266 nm resulted in one order of magnitude smaller pulse energy compared to the default pulse. Consequently, the fs-laser wavelength of 266 nm was only available with

reduced laser power and hence not comparable for the whole power density range covered by the fs-laser at 800 nm and the excimer laser at 193 nm, and we were only able to acquire a reduced number of spectra compared to the settings at higher power densities. We have added the following information to the main manuscript:

- *Section 2.2: "We also used a third harmonic generation module (Spectra Physics, TP-THG-F) to generate 266 nm pulses of 0.2 mJ and 100 fs duration. However, the resulting one order of magnitude smaller pulse energy of the laser compared to the default 800 nm wavelength led to a reduced light scattering signal, corresponding ineffective triggering of mass spectra recording, and thus reduced particle detection and lower ion signal. We therefore focus our analysis in this manuscript on fs-laser spectra at 800 nm wavelength."*
- *Section 3.1.7: "A discussion on single particle mass spectra for 266 nm (fs-laser) in comparison with those obtained using 193 nm (ns-laser) and 800 nm (fs-laser) is presented in the SI (Figs S7 - S13)."*

Using 800 nm for LDI seems a poor choice since so many particle components will absorb poorly in the near IR. There are few good chromophores here, and the wavelength is not long enough to access most vibrational modes, as is done using a 10.6 micron CO2 laser for two-step LDI, for example (Morrical et al., 1998; Zelenyuk et al., 2008). So the fact that the mass spectra obtained from 266 and 800 nm LDI are so similar is surprising. I would think that the particle hit rate would be much higher for 266 vs. 800 nm, but this is hard to quantify using the free-fired laser and the unreliable particle detection by light scattering from the laser pulse. Indeed the very different particle detection scheme when using the fs vs. ns laser makes a direct comparison of the performance of these two types of lasers almost impossible, which is most unfortunate. These issues should be discussed more fully, especially in regard to how the laser wavelength influences how the particle interacts with the photons.

Also, it is often not clear what wavelength is being discussed for the fs laser. 800 nm appears to be the default? Please clarify. Also, why is so much more emphasis placed on the 800 nm fs results and not on the 266 nm fs results? Since 266 nm LDI is commonly used for SP-MS by the ATOFMS, for example, a direct comparison at the same wavelength for the fs and a ns 266 nm laser would be possible by comparing to reported ATOFMS spectra. Why was this not done? My main concern here is that the laser wavelength is a critical variable and its important role is not being properly considered and discussed in the manuscript.

Compare previous response. Indeed the fs-laser has a default wavelength of 800 nm with 3.5 mJ maximum energy per pulse. We used a third harmonic generation module from Spectra Physics® (model TP-THG-F) to generate 266 nm pulses with 0.2 mJ maximum puls energy and 100 fs pulse duration. We now state clearly in the manuscript (section 2.2) that 800 nm is the default wavelength and at the focus of our analyses, due to the limited detection of spectra at 266 nm. We have added a new section to the SI (Figs. S7 – S13) that discusses the spectral patterns at 266 nm fs-laser wavelength (based on limited data) compared to 800 nm fs-laser and 193 nm ns-laser spectra. We observed some differences in the mass spectra for 266 and 800 nm, like less intense narrow peaks and less background signals for 266 nm; however, the major spectral patterns are surprisingly similar.

In contrast to the 266 nm fs pulses with <0.2 mJ, the ATOFMS typically uses 266 nm ns pulses with much higher energy (~5 mJ). However, we have added a discussion of typical results from ATOFMS for different samples to the SI.

There are several earlier reports of using two-step LDI for SP-MS that should be included and discussed. Passig et al. is an interesting and recent approach but is certainly not the first. Note that the Zelenyuk

group has using two-step LDI for depth profiling. (Morrical et al., 1998; Smith et al., 2002; Sykes et al., 2002; Whiteaker and Prather, 2003; Woods et al., 2002; Zelenyuk et al., 2008).

Of course two-step LDI is an interesting method to e.g. to obtain molecular ion information from complex organic mixtures. However, focus of this work was to study the potential of using an fs-laser in a single step LDI process. We consider it therefore reasonable to limit ourselves to the discussion of single step LDI, but have added the following section to the introduction. "The absorption of photons depends on the optical properties of the chemical components of the particle, with important implications for core-shell or multi-component particles (Cahill et al., 2015). Reported approaches for improvement of the quantitative abilities of SPMS include e.g. two step vaporization-ionization, where a CO_2 laser was used prior to excimer laser ionization for the evaporation of the particles (Cabalo et al., 2000; Morrical et al., 1998; Smith et al., 2002; Whiteaker and Prather, 2003; Woods et al., 2002), or the use of a high power density Nd:YAG laser of 5 ns pulse duration with 100 mJ pulse energy (> 1010 W m-2) (Lee et al., 2005; Mahadevan et al., 2002; Zhou et al., 2007)."

As particle detection for laser triggering is an important aspect of SP-MS (the use of a free fired fs laser here results in a low level of mass spectral reproducibility), more information on how the ns excimer laser is triggered would be useful. It is my understanding that the design of the LAAPTOF's particle detection system by laser light scattering has rather poor performance, with low particle detection rates < 500 nm diameter. There have also been several different attempts to improve the particle detection scheme. Please describe what particle detection scheme is used here (and if it is similar to that used in other LAAPTOF-based papers), and what its typical performance is (i.e. particle detection rate as a function of particle size).

Considering the difficulties to couple a free firing fs-laser to a single particle mass spectrometer, we did achieve a rather good reproducibility of the mass spectra as is demonstrated in Figs S3-S5. The particle detection system of the LAAPTOF was described and shown to have a reasonable performance in a recent publication by Shen et al. (2018) for the LAAPTOF instrument used in this study. To emphasize this, we have added the following text to section 2.1: " The particle size detection methods and detection efficiencies of the LAAPTOF have been described in several publications (Gemayel et al., 2016; Marsden et al., 2016; Shen et al., 2018). Shen at al. (2018) show a comparison of the performance of the instrument we used in this study with other and modified LAAPTOF instruments."

Line 61: While quantification vis SP-MS is challenging, this has been successfully demonstrated several times, especially if you confine the analysis to particles of a similar type, which reduces variability caused by particle matrix effects. The SP-MS response can also be calibrated using other co-located measurements. This paragraph should be expanded to more accurately reflect what can be achieved by LDI SP-MS analysis. Some examples: (Bhave et al., 2002; Fergenson et al., 2001; Gross et al., 2000, 2005; Healy et al., 2013; Saul et al., 2006; Sullivan et al., 2007, 2009)

Several studies have demonstrated progress towards quantification with SPMS. However, there are still limitations. Quantification is also more difficult to achieve for online measurements of a wide range of particle types and complex mixtures as typical for the atmosphere. To better reflect previous work about quantitative SPMS we have added the following sentences to the introduction: "Quantitative analysis of single aerosol particles via laser ablation remains challenging, although, several studies achieved advancements (Bhave et al., 2001; Fergenson et al., 2001; Gross et al., 2005; Healy et al., 2013), e.g. by detailed characterization of instrument sensitivity for individual chemical species, and by optimizing ionization laser parameters to reduce fragmentation. However, so far no single particle mass spectrometer is available for quantitative on-line analysis of particle mixtures."

The emphasis on excimer laser-based SP-MS instruments while ignoring Nd:YAG (266 nm) SP-MS instruments was odd to me, especially since a 266 nm fs laser is used here. There are lots of 266 nm SP-MS spectra you could compare to.

Indeed we did not sufficiently compare our results to the results of SPMS instruments like the ATOFMS with a 266 nm Nd:YAG ionization laser. As said earlier, we focus on the comparison of the 193 nm ns-laser with the 800 nm fs-laser data because of the limited range of pulse energy available for the 266 nm fs-laser, and the surprisingly similar mass spectra obtained for both wavelengths of the fs laser. We have now added several plots to the SI comparing mass spectra for LDI at 193 nm, 266 nm, and 800 nm (Figs S7 – S13), the discussion of which also includes data from Nd:YAG (266 nm) SPMS instruments.

One missing example is the study of LDI of Au metal nanoparticles using a tunable visible laser coupled to an ATOFMS (Spencer et al., 2008). They discussed the importance of the surface plasmon effect for LDI of metal nanoparticles.

Thank you for pointing to the work of Spencer et al. (2008). We have added the reference to the discussion on spectra as a function of laser wavelengths in the SI: "The core-shell particle mass spectra we obtained with 193 nm ns-laser show quite some similarity with the mass spectra observed by Spencer et al. (2008) for gold nanoparticles with a 266 nm nanosecond ATOFMS .However, for fs laser pulses of both 266 nm and 800 nmn we haven't observed any signals from the gold core." The LDI process is explained in the supplementary section. Our results show that highly reflective surfaces can reduce the spectral signatures from the core. In addition, desorption of particle surface material with different pulse durations can generate different mass spectra due to thermal and shielding effects.

Schoolcraft et al. performed MD simulations of the LDI laser ablation process (Schoolcraft et al., 2000, 2001).

Molecular dynamic simulation studies for laser desorption and ionization are discussed in the introduction of our manuscript. We have added the suggested references to the introduction as following: "Molecular dynamic model simulations by Schoolcraft et al. (2001, 2000) explained the process of laser desorption and ionization of submicron particles for amorphous and crystalline particles with and without inclusions (Schoolcraft et al., 2001; Schoolcraft et al., 2000) as a function of the nature of the material. "

Line 300: Is this for 800 nm or 266 nm fs laser? The low hit rate for NH4NO3 particles would be expected using 800 nm laser as these particles are weakly absorbing even in the UV.

This is for 800 nm fs-laser pulses. The qualitative hit rate is small with both wavelengths of the fs-laser. We have added the wavelength in the text.

Sect. 3.2: The ion signal response versus particle size is certainly worth exploring and important, but you would have to test more than just two particle sizes of the same particle matrix to really conclude anything meaningful here. Why were more particle sizes explored?

We have measured three different particle sizes with PSLs, 500 nm, 800 nm and 1000 nm. We have shown only results for 500 nm and 1000 nm to demonstrate the maximum impact. However, the results for PSL particles of 800 nm diameter are in between the intensities for 500 nm and 1000nm particle diameters.

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